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PATENT ABSTRACTS OF JAPAN

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(54) GLASS SUBSTRATE FOR MAGNETIC DISK AND MAGNETIC DISK

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain a glass substrate for a magnetic disk less liable to scuffing and breaking and to inhibit the corrosion of a metallic magnetic film on the glass substrate by chemically strengthened glass having a specified compsn. consisting of SiO_2, Al_2O_3, alkali metallic oxides, alkaline earth metallic oxides and ZrO_2.
SOLUTION: Glass having a compsn. consisting essentially of, by weight, 60-70% SiO_2, 1-12% Al_2O_3, 1-7% Na_2O, 9-16% K_2O ($10\% \leq Na_2O+K_2O \leq 17\%$), 8-17% MgO+CaO+CrO+BaO and 0.5-5% ZrO_2 is chemically strengthened by immersion in a potassium nitrate or potassium nitrate-sodium nitrate mixed soln. at 400-530° C for 1-20hr to form a compressive stress layer having ≥5 ì m thickness from the surface of the glass and the objective glass substrate is obtd. using the resultant glass.

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CLAIMS

[Claim(s)]
[Claim 1] A presentation substantially by weight % display SiO2 60-70, aluminum 2O3 1-12, and Na2 O 1- 7, K2 O 9-16, Na2 O+K2 O -- 10-17, and MgO+CaO+SrO+BaO 8-17, and ZrO2 0.5- 5 -- since -- glass substrate for magnetic disks which comes to carry out chemical-strengthening processing of the becoming glass.
[Claim 2] The glass substrate for magnetic disks according to claim 1 whose consistency is 2.7g/cc or less.
[Claim 3] The glass substrate for magnetic disks according to claim 1 or 2 whose brittleness index value is 1/2 or less [7400m -].
[Claim 4] A presentation substantially by weight % display SiO2 60-70, aluminum 2O3 1- 7, Na2 O 1- 7, K2 O 9-16, Na2 O+K2 O 10-17, MgO 0.5- 9 CaO 0.5-10, SrO 0- 5 and BaO 0- 2 and MgO+CaO 5-13, and ZrO2 0.5- 5 -- since -- becoming glass substrate for magnetic disks according to claim 1, 2, or 3.
[Claim 5] A presentation substantially by weight % display SiO2 60-70, aluminum 2O3 1- 7, Na2 O 1- 7, K2 O 12-16, Na2 O+K2 O 13-17, MgO 1- 7 CaO 1- 8 SrO 0- 3 and BaO 0- 1 and MgO+CaO 6-13, and ZrO2 0.5- 4 -- since -- becoming glass substrate for magnetic disks according to claim 1, 2, 3, or 4.
[Claim 6] The glass substrate for magnetic disks according to claim 1, 2, 3, 4, or 5 which has a compressive-stress layer with a thickness of 5 micrometers or more from a front face.
[Claim 7] The glass substrate for magnetic disks according to claim 1, 2, 3, 4, 5, or 6 characterized by carrying out chemical-strengthening processing by immersing glass in the mixed liquor of a 400-530-degree C potassium nitrate, or a this and a sodium nitrate for 1 to 20 hours.
[Claim 8] The magnetic disk which comes to prepare a substrate layer, a magnetic layer, a protective layer, and a lubricating layer one by one on the glass substrate for magnetic disks according to claim 1, 2, 3, 4, 5, 6, or 7.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the glass substrate for magnetic disks, and a magnetic disk.
[0002]
[Description of the Prior Art] As for a magnetic disk, a magnetic film and a protective coat are formed of processes, such as a spatter, plating, and vacuum evaporationo, on a substrate, and, generally it is observed as an ingredient of the substrate for magnetic disks which fitted densification from the reasons of glass being excellent in surface smooth nature, and being hard, and its deformation resistance being large, and there being little surface discontinuity.
[0003] When the glass containing alkali comparatively cheap as a glass substrate, for example, soda lime silica glass, is used, and the bottom of a humid environment and ageing processing are carried out especially, it is found out that alkali ion deposits from the part which a part or glass with thin magnetic films, such as the pinhole section of a magnetic film or a periphery of a magnetic film, exposed, this serves as a trigger, and a magnetic film corrodes or discolors.
[0004] Moreover, compared with substrates, such as the conventional aluminium alloy, disruptive strength of a glass substrate is low. Therefore, existence of few blemishes formed at the time of wearing and the other handling by the spindle leads to breakage.

[0005] Therefore, although giving a chemical strengthening to a glass substrate and forming a compressive-stress layer in a front face is performed, just it is inadequate in many cases.
[0006]
[Problem(s) to be Solved by the Invention] The purpose of this invention solves the above-mentioned fault, and it is to offer the glass substrate which a blemish cannot attach easily and cannot damage easily while it improves the corrosion of the metal magnetic film on the glass substrate which had become a problem by the conventional soda lime glass silica.
[0007]
[Means for Solving the Problem] A presentation substantially by weight % display SiO2 60-70, aluminum 2O3 1-12, and Na2 O 1-7, K2 O 9-16, Na2 O+K2 O -- 10-17, and MgO+CaO+SrO+BaO 8-17, and ZrO2 0.5- 5 -- since -- it is the glass substrate for magnetic disks which comes to carry out chemical-strengthening processing of the becoming glass.
[0008]
[Embodiment of the Invention] The presentation of the glass in this invention is explained below. SiO2 It is the network former of glass and may be 60 - 70 % of the weight in this invention. If there is little this, it will become easy to attach a blemish and chemical durability will fall. When many [too], there is an inclination for the dissolution to become difficult. It is 62 - 68 % of the weight more preferably.
[0009] aluminum 2O3 While raising the chemical durability of glass, the rate of the ion exchange which permutes the alkali metal of the glass surface section with alkali metal with a more large ionic radius is increased, there is an operation carried out that it is easy to make deep compressive stress form, and it may be 1 - 12 % of the weight in this invention. The dissolution will become difficult if there is too much this. It is 7 or less % of the weight more preferably.
[0010] Na2 O becomes the main component by which the ion exchange is carried out at the time of a chemical strengthening while it lowers the viscosity at the time of the glass dissolution and promotes the dissolution. In this invention, it may be 1 - 7 % of the weight. When there is too much this, it is chemical durability not only falling but Na+. In order for many ion to deposit to a glass substrate front face, there is a possibility that the corrosion resistance of a magnetic film may deteriorate. It is 4 or less % of the weight preferably.
[0011] Addition of K2 O raises the rate of the ion exchange at the time of a chemical strengthening. Moreover, by permuting a part of Na2 O, the addition of Na2 O is reduced and the corrosion resistance of a magnetic film can be raised. Conversely, if K2 O increases and Na2 O decreases too much relatively, the ion exchange itself will stop being able to happen easily. The addition of K2 O is made into 9 - 16 % of the weight in this invention. It is the viewpoint which makes the ion exchange easy, and K2 O is 13 % of the weight or more 12% of the weight or more especially preferably. Moreover, K2 O+Na2 O is the above viewpoint and may be 10 - 17 % of the weight.
[0012] MgO, CaO, SrO, and BaO lower the viscosity at the time of the glass dissolution, and in order to make it easy to dissolve, they contain it 8% of the weight or more with a total amount. It is 13 % of the weight or more in a total amount preferably. On the other hand, when it exceeds 17 % of the weight with a total amount, there is an inclination for glass to become easy to get damaged and for devitrification temperature to become high.
[0013] In order to make shaping by the float glass process easy, especially MgO considers as 1 - 7 % of the weight 0.5 to 9% of the weight, and especially CaO considers as 1 - 8 % of the weight 0.5 to 10% of the weight, and, as for especially MgO+CaO, it is desirable to consider as 6 - 13 % of the weight five to 13% of the weight. When there are too much these, there is a possibility that devitrification temperature may become high and shaping by the float glass process may become difficult.
[0014] SrO can be added a sake [on a dissolution disposition], although it is not indispensable. Especially in order to make shaping by the float glass process easy, it is desirable to consider as 0 - 3 % of the weight zero to 5% of the weight. If there is too much this, devitrification temperature will become high, and there is a possibility that glass may become easy to get damaged.
[0015] It is desirable to be able to add a sake [on a dissolution disposition], although BaO is not indispensable, either, and to consider as 0 - 2 % of the weight. When there is also too much this, devitrification temperature becomes high and there is a

possibility that glass may become easy to get damaged.
[0016] ZrO2 It is effective in raising chemical durability. In this invention, it may be 0.5 - 5 % of the weight. In respect of the improvement in chemical durability, it contains 2% of the weight or more preferably. On the other hand, when many [too], dissolution nature falls and there is a possibility that glass may become easy to get damaged. It is 4 or less % of the weight preferably.
[0017] The glass substrate by this invention is As 2O3, Sb 2O3, P2 O5, and F, Cl and SO3, in order to improve the dissolution nature of glass, clarity, and a moldability in addition to the above-mentioned component. It can add 2 or less % of the weight with a total amount. Moreover, it is La 2O3, TiO2, SnO2, and B-2 O3 because of the improvement in chemical durability of glass. It can add 5 or less % of the weight with a total amount. Moreover, although ZnO can also be added for the improvement in chemical durability, in order not to spoil a float moldability, it is desirable to consider as 1 or less % of the weight. ZnO is not contained especially substantially preferably.
[0018] Furthermore, coloring matters, such as Fe 2O3, CoO, NiO and Nd 2O3, and Se, are added, and the color tone of glass can be adjusted. The content of this coloring matter has 1 or less desirable % of the weight at a total amount. In addition, alkali components, such as K2 O and Na2 O, can permute an amount by Li2 O a little [this]. The content of Li2 O has 3 or less desirable % of the weight.
[0019] The brittleness index value B proposed by loans as an index value which shows the brittleness of glass in this invention is used (B. R.Lawn and D.B.Marshall, J.Am.Ceram.Soc., and 62 (7-8) 347-350 (1979)). here -- the brittleness index value B -- Vickers hardness number HV of an ingredient Fracture toughness value KC from -- several 1 defines.
[0020]
[Equation 1] B=HV /KC (1)
[0021] As for the brittleness index value of the glass of this invention, it is desirable that it is 1/2 or less [7400m -], and it is 1/2 or less [7300m -] more preferably. Moreover, a chemical strengthening is possible for the glass of this invention. A chemical strengthening is usually performed by immersing a glass plate in potassium-nitrate melt or the mixed melt of a potassium nitrate and a sodium nitrate. Especially in the glass of this invention, 5 micrometers or more of compression-pressure layers with a thickness of 10 micrometers or more can be produced from a front face according to a chemical strengthening.
[0022] As mentioned above, in being hard to attach a blemish, since the conventional glass for magnetic disks and the chemical strengthening more than equivalent are possible for the glass of this invention, it can reduce breakage fear in use sharply as the inside of a production process, and a product. In addition, 2.7g/cc or less of consistencies of the glass of this invention is 2.6g/cc or less especially typically. This also makes the impact at the time of fall small, and makes fear of breakage small.
[0023] Moreover, float shaping is sometimes possible as one important description of the glass of this invention. Namely, 104 which is the molding temperature at the time of float shaping Compared with the temperature which shows the viscosity of a poise, devitrification temperature is low. Therefore, float shaping is possible, without producing faults, such as devitrification.
[0024] The glass of this invention can be manufactured by the following approaches, for example. That is, the raw material of each component usually used is prepared so that it may become a target component, this is continuously supplied to a fusion furnace, and it heats and fuses at 1500-1600 degrees C. This melting glass is fabricated to predetermined board thickness with a float glass process, and is cut after annealing.
[0025] In the glass substrate of this invention, chemical-strengthening processing of the glass plate cut by predetermined size is carried out. What is necessary is just to perform chemical-strengthening processing by the well-known approach. That is, it can carry out by taking out, after glass goods are immersed in the mixed liquor of a 400-530-degree C potassium nitrate, or a this and a sodium nitrate for about 2 to 20 hours, and cooling slowly.
[0026] What is necessary is just to prepare a substrate layer, a magnetic layer, a protective layer, and a lubricating layer one by one on a glass substrate with the glass substrate for magnetic disks of this invention, in order to form a magnetic disk.
[0027] As a magnetic layer as a magnetic-recording layer used by this invention, Co system alloys, such as a Co-Cr system, a Co-Cr-Pt system, a Co-nickel-Cr system, a Co-nickel-Cr-Pt system, a Co-nickel-Pt system, and a Co-Cr-Ta system, are preferably employable. As a substrate layer prepared in the bottom of a magnetic layer in order to improve endurance and magnetic properties, it is nickel layer, a nickel-P layer, Cr layer, and SiO2. A layer etc. is employable.
[0028] In this invention, the metal or alloy layer which consists of Cr layer, a Cr alloy layer, and other ingredients can be prepared on a magnetic layer or in the bottom.
[0029] In order to be able to use carbon with a thickness of 50-1000A or the layer of a silica and to form a lubricating layer as a protective layer, the fluid lubrication agent of a perfluoro polyether system with a thickness of about 30A can be used.
[0030]
[Example]
According to the conventional method, it prepared and mixed about four kinds of presentations of Examples 1-4 shown in the <creation of tabular glass> table 1, and the glass batch was prepared. Subsequently, the glass batch was put into Pt-Rh10% crucible with a capacity of about 500ml, and it melted for about 4 hours including churning of about 1 hour for homogenization at 1500 degrees C, was beginning to pass on the carbon plate, and considered as tabular, and after annealing, it cut and ground according to the conventional method, and the tabular glass sample of about 1mm thickness was obtained. In addition, Examples 1-5 are examples and Examples 6 and 7 are examples of a comparison.
[0031] The devitrification temperature of these glass, and 104 The temperature of a poise, and 102 The temperature of a poise, strain point temperature, and a brittleness index value were measured, and it wrote together to Table 1. Subsequently, the tabular glass sample of Examples 1-5 was cut and ground, and it created each 20 circular glass disk substrates of the shape of a doughnut with the outer diameter of 65mm, a bore [of 20mm], and a thickness of 0.635mm.
[0032] The brittleness index value (unit: m-1/2) was calculated as follows. The big problem at the time of applying a brittleness index value to glass is the fracture toughness value KC. It is hard to evaluate correctly. However, as a result of examining some technique, these people have found out that brittleness can be quantitatively evaluated from the relation between the magnitude of the marks of the indenter which remains in a glass front face, and the die length of the crack generated from the four corners of marks, when the Vickers indenter is pushed in. The relational expression is defined by the formula (2). Here, P is the pushing load of the Vickers indenter and a and c are the die length (overall length of two symmetrical cracks containing the marks of an indenter) of the crack generated from the diagonal length and four corners of the Vickers indentation, respectively. A brittleness index value is evaluated using the dimension of the Vickers indentation driven into the front face of various glass, and several 2.
[0033]
[Equation 2]

c/a=0.0056B2/3 P1/6 (2)
[0034] The probability for a blemish to damage the glass substrate of Example 7 at the time of rotation that it is easy to attach since a brittleness index value exceeds −1/2 7400m will be large.
[0035] It performed chemical-strengthening processing each about ten substrates of the <chemical-strengthening nature test> above-mentioned glass disk. That is, about Examples 1-4 and Example 7, it was immersed in the 480-degree C melting potassium-nitrate salt, and was immersed in the 450-degree C melting potassium-nitrate salt about Example 6 for 10 hours, respectively, and chemical-strengthening processing was performed. About each above-mentioned glass disk substrate, the result of having measured the thickness of a surface pressure shrinkage stress layer in main surface stress meter FSW-60 made from Toshiba glass is written together to Table 1. The glass substrate by this invention can produce a compressive-stress layer 10 micrometers or more so that clearly from a table.
[0036] It is a spatter on each main front face of <moisture-proof test of magnetic-recording medium> above-mentioned a non-strengthened article and, and a strengthening article. After forming the substrate layer which consists of Cr with a thickness of about 500A, the Co-30 atom %nickel alloy magnetic layer with a thickness of about 600A was formed, the carbon protective coat with a thickness of about 300A was formed on it, and the magnetic-recording medium was obtained by applying the fluid lubrication agent of a perfluoro polyether system on it further. The moisture-proof test was carried out by holding on 80 degrees C and the ambient atmosphere conditions of 90%RH about these for 100 hours.
[0037] The brittleness index value of the glass substrate by this invention is 1/2 or less [7400m −], and a blemish cannot attach it easily so that more clearly than a table. Therefore, there are no problems, like breakage takes place at the time of rotation that it is hard to attach a blemish at the time of wearing and the other handling by the spindle. Furthermore, as for the magnetic-recording medium which consists of a glass substrate of Examples 1-5, non-strengthened elegance and a strengthening article were not accepted for discoloration. Moreover, devitrification temperature is 104 which is the shaping viscosity of a float glass process. It turns out that it is lower than the temperature equivalent to a poise, and suitable for manufacture by the float glass process.
[0038] On the other hand, discoloration was accepted having covered in the field the non-strengthened elegance magnetic-recording medium which consists of a glass substrate of Example 6 from the interface of a Co-nickel alloy layer and glass over the range of 2-3mm from the end face of the inner circumference of a disk, and a periphery, and, similarly discoloration was accepted over the range of 1-2mm by the strengthening article magnetic-recording medium which consists of a glass substrate of Example 6.
[0039]
[Table 1]

	例1	例2	例3	例4	例5	例6	例7
SiO_2	65.2	61.7	67.4	63.0	64.2	72.5	48.5
Al_2O_3	4.0	9.4	4.1	6.7	6.7	1.5	14.8
Na_2O	1.9	5.5	4.9	3.4	1.4	13.5	5.3
K_2O	14.1	9.2	10.2	12.2	13.5	0.5	6.5
MgO	4.4	3.6	4.5	3.3	3.6	4.0	3.8
CaO	7.0	4.9	7.2	6.9	7.2	8.0	6.6
SrO	-	1.6	0.4	3.2	2.9	—	7.0
BaO	-	1.2	-	0.6	—	—	5.5
ZrO_2	3.4	2.9	1.3	0.7	0.5	—	2.0
Fe_2O_3	0.1	-	-	-	—	0.1	—
Na_2O+K_2O	16.0	14.7	15.1	15.6	14.9	14.0	11.8
MgO +CaO +SrO +BaO	11.4	11.3	12.1	14.0	13.7	12.0	22.9
MgO +CaO	11.4	8.5	11.7	10.2	10.8	12.0	10.4
失透温度（℃）	1140	1163	1120	1138	1159	980	1180
10^4 ポイズの温度（℃）	1192	1187	1138	1147	1185	1040	1046
10^2 ポイズの温度（℃）	1590	1618	1578	1578	1616	1460	1444
ガラス転移点（℃）	657	647	623	633	658	540	636
脆さ指標値	7200	7300	7200	7200	7100	7100	7800
圧縮応力層厚さ（μm）	10	13	14	13	12	20	18
密度（g／cc）	2.52	2.55	2.49	2.53	2.51	2.49	2.77
耐湿テストによる変色	無	無	無	無	有	有	無

[0040]
[Effect of the Invention] Compared with the glass substrate which used soda lime silica glass, a blemish cannot attach the high intensity this invention glass substrate for magnetic disks easily, and corrosion resistance and aging-proof nature are extremely

excellent. Furthermore, the glass substrate for magnetic disks of this invention also fits shaping by the float glass process.

[Translation done.]

TECHNICAL FIELD

[Field of the Invention] This invention relates to the glass substrate for magnetic disks, and a magnetic disk.

[Translation done.]

PRIOR ART

[Description of the Prior Art] As for a magnetic disk, a magnetic film and a protective coat are formed of processes, such as a spatter, plating, and vacuum evaporationo, on a substrate, and, generally it is observed as an ingredient of the substrate for magnetic disks which fitted densification from the reasons of glass being excellent in surface smooth nature, and being hard, and its deformation resistance being large, and there being little surface discontinuity.
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EFFECT OF THE INVENTION

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] The purpose of this invention solves the above-mentioned fault, and it is to offer the glass substrate which a blemish cannot attach easily and cannot damage easily while it improves the corrosion of the metal magnetic film on the glass substrate which had become a problem by the conventional soda lime glass silica.

[Translation done.]

MEANS

[Means for Solving the Problem] A presentation substantially by weight % display SiO2 60-70, aluminum 2O3 1-12, and Na2 O 1-7, K2 O 9-16, Na2 O+K2 O — 10-17, and MgO+CaO+SrO+BaO 8-17, and ZrO2 0.5- 5 — since -- it is the glass substrate for magnetic disks which comes to carry out chemical-strengthening processing of the becoming glass.
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EXAMPLE

[Example]
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[0035] It performed chemical-strengthening processing each about ten substrates of the <chemical-strengthening nature test> above-mentioned glass disk. That is, about Examples 1-4 and Example 7, it was immersed in the 480-degree C melting potassium-nitrate salt, and was immersed in the 450-degree C melting potassium-nitrate salt about Example 6 for 10 hours, respectively, and chemical-strengthening processing was performed. About each above-mentioned glass disk substrate, the result of having measured the thickness of a surface pressure shrinkage stress layer in main surface stress meter FSW-60 made from Toshiba glass is written together to Table 1. The glass substrate by this invention can produce a compressive-stress layer 10 micrometers or more so that clearly from a table.
[0036] It is a spatter on each main front face of <moisture-proof test of magnetic-recording medium> above-mentioned a non-strengthened article and, and a strengthening article. After forming the substrate layer which consists of Cr with a thickness of about 500A, the Co-30 atom %nickel alloy magnetic layer with a thickness of about 600A was formed, the carbon protective coat with a thickness of about 300A was formed on it, and the magnetic-recording medium was obtained by applying the fluid lubrication agent of a perfluoro polyether system on it further. The moisture-proof test was carried out by holding on 80 degrees C and the ambient atmosphere conditions of 90%RH about these for 100 hours.
[0037] The brittleness index value of the glass substrate by this invention is 1/2 or less [7400m -], and a blemish cannot attach it easily so that more clearly than a table. Therefore, there are no problems, like breakage takes place at the time of rotation that it is hard to attach a blemish at the time of wearing and the other handling by the spindle. Furthermore, as for the magnetic-recording medium which consists of a glass substrate of Examples 1-5, non-strengthened elegance and a strengthening article were not accepted for discoloration. Moreover, devitrification temperature is 104 which is the shaping viscosity of a float glass process. It turns out that it is lower than the temperature equivalent to a poise, and suitable for manufacture by the float glass process.
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[0039]
[Table 1]

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SiO_2	65.2	61.7	67.4	63.0	64.2	72.5	48.5
Al_2O_3	4.0	9.4	4.1	6.7	6.7	1.5	14.8
Na_2O	1.9	5.5	4.9	3.4	1.4	13.5	5.3
K_2O	14.1	9.2	10.2	12.2	13.5	0.5	6.5
MgO	4.4	3.6	4.5	3.3	3.6	4.0	3.8
CaO	7.0	4.9	7.2	6.9	7.2	8.0	6.6
SrO	-	1.6	0.4	3.2	2.9	—	7.0
BaO	-	1.2	-	0.6	—	—	5.5
ZrO_2	3.4	2.9	1.3	0.7	0.5	—	2.0
Fe_2O_3	0.1	-	-	-	—	0.1	—
Na_2O+K_2O	16.0	14.7	15.1	15.6	14.9	14.0	11.8
MgO +CaO +SrO +BaO	11.4	11.3	12.1	14.0	13.7	12.0	22.9
MgO +CaO	11.4	8.5	11.7	10.2	10.8	12.0	10.4
失透温度（℃）	1140	1163	1120	1138	1159	980	1180
10^4 ポイズの温度（℃）	1192	1187	1138	1147	1185	1040	1046
10^2 ポイズの温度（℃）	1590	1618	1578	1578	1616	1460	1444
ガラス転移点　（℃）	657	647	623	633	658	540	636
脆さ指標値	7200	7300	7200	7200	7100	7100	7800
圧縮応力層厚さ（μm）	10	13	14	13	12	20	18
密度（g／cc）	2.52	2.55	2.49	2.53	2.51	2.49	2.77
耐湿テストによる変色	無	無	無	無	有	有	無

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[Table 1]

	例1	例2	例3	例4	例5	例6	例7
SiO_2	65.2	61.7	67.4	63.0	64.2	72.5	48.5
Al_2O_3	4.0	9.4	4.1	6.7	6.7	1.5	14.8
Na_2O	1.9	5.5	4.9	3.4	1.4	13.5	5.3
K_2O	14.1	9.2	10.2	12.2	13.5	0.5	6.5
MgO	4.4	3.6	4.5	3.3	3.6	4.0	3.8
CaO	7.0	4.9	7.2	6.9	7.2	8.0	6.6
SrO	−	1.6	0.4	3.2	2.9	−	7.0
BaO	−	1.2	−	0.6	−	−	5.5
ZrO_2	3.4	2.9	1.3	0.7	0.5	−	2.0
Fe_2O_3	0.1	−	−	−	−	0.1	−
Na_2O+K_2O	16.0	14.7	15.1	15.6	14.9	14.0	11.8
MgO＋CaO＋SrO＋BaO	11.4	11.3	12.1	14.0	13.7	12.0	22.9
MgO ＋CaO	11.4	8.5	11.7	10.2	10.8	12.0	10.4
失透温度（℃）	1140	1163	1120	1138	1159	980	1180
10^4 ポイズの温度（℃）	1192	1187	1138	1147	1185	1040	1046
10^2 ポイズの温度（℃）	1590	1618	1578	1578	1616	1460	1444
ガラス転移点（℃）	657	647	623	633	658	540	636
脆さ指標値	7200	7300	7200	7200	7100	7100	7800
圧縮応力層厚さ（μm）	10	13	14	13	12	20	18
密度（g／cc）	2.52	2.55	2.49	2.53	2.51	2.49	2.77
耐湿テストによる変色	無	無	無	無	無	有	無

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(54)【発明の名称】磁気ディスク用ガラス基板および磁気ディスク

(57)【要約】

【課題】傷がつきにくく、かつガラス基板上の金属磁性膜の腐食を改善するガラス基板を提供する。

【解決手段】組成が重量％表示で実質的にSiO_2：６０～７０、Al_2O_3：１～１２、Na_2O：１～７、K_2O：９～１６、Na_2O+K_2O：１０～１７、$MgO+CaO+SrO+BaO$：８～１７、ZrO_2：０．５～５、であるガラスを化学強化処理してなる磁気ディスク用ガラス基板。

１

【特許請求の範囲】

【請求項１】組成が重量％表示で実質的に、

SiO_2	６０～７０、
Al_2O_3	１～１２、
Na_2O	１～　７、
K_2O	９～１６、
Na_2O+K_2O	１０～１７、
$MgO+CaO+SrO+BaO$	８～１７、
ZrO_2	０．５～　５、から

なるガラスを化学強化処理してなる磁気ディスク用ガラス基板。

【請求項２】密度が２．７ｇ／ｃｃ以下である請求項１記載の磁気ディスク用ガラス基板。

【請求項３】脆さ指標値が７４００$m^{-1/2}$以下である請求項１または２記載の磁気ディスク用ガラス基板。

【請求項４】組成が重量％表示で実質的に、

SiO_2	６０～７０、
Al_2O_3	１～　７、
Na_2O	１～　７、
K_2O	９～１６、
Na_2O+K_2O	１０～１７、
MgO	０．５～　９、
CaO	０．５～１０、
SrO	０～　５、
BaO	０～　２、
$MgO+CaO$	５～１３、
ZrO_2	０．５～　５、

からなる請求項１、２または３記載の磁気ディスク用ガラス基板。

【請求項５】組成が重量％表示で実質的に、

SiO_2	６０～７０、
Al_2O_3	１～　７、
Na_2O	１～　７、
K_2O	１２～１６、
Na_2O+K_2O	１３～１７、
MgO	１～　７、
CaO	１～　８、
SrO	０～　３、
BaO	０～　１、
$MgO+CaO$	６～１３、
ZrO_2	０．５～　４、

からなる請求項１、２、３または４記載の磁気ディスク用ガラス基板。

【請求項６】表面から５μｍ以上の厚さの圧縮応力層を有する請求項１、２、３、４または５記載の磁気ディスク用ガラス基板。

【請求項７】４００～５３０℃の硝酸カリウムまたはこれと硝酸ナトリウムとの混合液にガラスを１～２０時間浸漬することによって化学強化処理されていることを特徴とする請求項１、２、３、４、５または６記載の磁気ディスク用ガラス基板。

２

【請求項８】請求項１、２、３、４、５、６または７記載の磁気ディスク用ガラス基板の上に、順次、下地層、磁性層、保護層、潤滑層を設けてなる磁気ディスク。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は磁気ディスク用ガラス基板および磁気ディスクに関する。

【０００２】

【従来の技術】磁気ディスクは、基板の上にスパッタ、メッキ、蒸着等のプロセスにより磁性膜および保護膜が形成されたものであり、一般にガラスは表面の平滑性に優れ、硬く、変形抵抗が大きく、かつ表面欠陥が少ない等の理由から高密度化に適した磁気ディスク用基板の材料として注目されている。

【０００３】ガラス基板として比較的安価なアルカリを含むガラス、たとえばソーダライムシリカガラス、を用いた場合、特に多湿環境下やエイジング処理をした場合において磁性膜のピンホール部または磁性膜の周辺部など磁性膜が薄い部分またはガラスが露出した部分からアルカリイオンが析出し、これが引きがねとなって磁性膜が腐食または変色することが見出されている。

【０００４】また、ガラス基板は従来のアルミニウム合金等の基板に比べ破壊強度が低い。従って、スピンドルへの装着その他取扱い時において形成されるわずかな傷の存在が破損につながる。

【０００５】そのため、ガラス基板に化学強化を施し表面に圧縮応力層を形成することが行われているが、それだけでは不十分な場合が多い。

【０００６】

【発明が解決しようとする課題】本発明の目的は、上記欠点を解決し、従来のソーダライムガラスシリカで問題となっていたガラス基板上の金属磁性膜の腐食を改善するとともに、傷がつきにくく破損しにくいガラス基板を提供することにある。

【０００７】

【課題を解決するための手段】組成が重量％表示で実質的に、

SiO_2	６０～７０、
Al_2O_3	１～１２、
Na_2O	１～　７、
K_2O	９～１６、
Na_2O+K_2O	１０～１７、
$MgO+CaO+SrO+BaO$	８～１７、
ZrO_2	０．５～　５、

からなるガラスを化学強化処理してなる磁気ディスク用ガラス基板である。

【０００８】

【発明の実施の形態】本発明におけるガラスの組成について以下に説明する。SiO_2はガラスのネットワーク

フォーマーであり、本発明では、60～70重量％とする。これが少ないと傷がつきやすくなり、また化学的耐久性が低下する。多すぎると熔解が困難になる傾向がある。より好ましくは62～68重量％である。

【0009】Al_2O_3はガラスの化学的耐久性を向上させるとともに、ガラス表層部のアルカリ金属をよりイオン半径の大きいアルカリ金属で置換するイオン交換の速度を増大させ、深い圧縮応力を形成させやすくする作用があり、本発明では1～12重量％とする。これが多すぎると、熔解が困難になる。より好ましくは7重量％以下である。

【0010】Na_2Oはガラス熔解時の粘性を下げ、溶解を促進するとともに、化学強化時にイオン交換される主たる成分となる。本発明では、1～7重量％とする。これが多すぎると、化学的耐久性が低下するだけでなく、Na^+イオンがガラス基板表面へ多く析出するようになるため、磁性膜の耐食性が劣化するおそれがある。好ましくは4重量％以下である。

【0011】K_2Oの添加は化学強化時のイオン交換の速度を向上させる。また、Na_2Oを一部置換することにより、Na_2Oの添加量を低減させ、磁性膜の耐食性を高めうる。逆にK_2Oが多くなり、Na_2Oが相対的に少なくなりすぎると、イオン交換そのものが起こりにくくなる。本発明ではK_2Oの添加量は9～16重量％とする。イオン交換を容易にする観点で、K_2Oは好ましくは12重量％以上、特に13重量％以上である。また、K_2O+Na_2Oは以上の観点で、10～17重量％とする。

【0012】MgO、CaO、SrOおよびBaOはガラス熔解時の粘性を下げ、溶解しやすくするために合量で8重量％以上含有される。好ましくは合量で13重量％以上である。他方、合量で17重量％を超えるとガラスが傷つきやすくなり、また、失透温度が高くなる傾向がある。

【0013】フロート法による成形を容易にするためには、MgOは0．5～9重量％、特に1～7重量％とし、CaOは0．5～10重量％、特には1～8重量％とし、また$MgO+CaO$は5～13重量％、特には6～13重量％とすることが好ましい。これらが多すぎると、失透温度が高くなりフロート法による成形が困難になるおそれがある。

【0014】SrOは必須ではないが熔解性向上のために添加できる。フロート法による成形を容易にするためには、0～5重量％、特には0～3重量％とすることが好ましい。これが多すぎると失透温度が高くなり、ガラスが傷つきやすくなるおそれがある。

【0015】BaOも必須ではないが熔解性向上のために添加でき、0～2重量％とすることが好ましい。これも多すぎると、失透温度が高くなり、ガラスが傷つきやすくなるおそれがある。

【0016】ZrO_2は化学的耐久性を向上させる効果がある。本発明では0．5～5重量％とする。化学的耐久性向上の点で、好ましくは2重量％以上含有する。一方多すぎると、熔解性が低下し、ガラスが傷つきやすくなるおそれがある。好ましくは4重量％以下である。

【0017】本発明によるガラス基板は上記成分以外に、ガラスの熔解性、清澄性、成形性を改善するため、As_2O_3、Sb_2O_3、P_2O_5、F、Cl、SO_3を合量で2重量％以下添加できる。また、ガラスの化学的耐久性向上のため、La_2O_3、TiO_2、SnO_2、B_2O_3を合量で5重量％以下添加できる。またZnOも化学的耐久性向上のために添加できるが、フロート成形性を損なわないために1重量％以下とすることが好ましい。特に好ましくは、ZnOは実質的には含有されない。

【0018】さらに、Fe_2O_3、CoO、NiO、Nd_2O_3、Se等の着色材を添加してガラスの色調を調整できる。この着色材の含有量は合量で1重量％以下が好ましい。なお、K_2O、Na_2Oなどのアルカリ成分は、この若干量をLi_2Oに置換できる。Li_2Oの含有量は3重量％以下が好ましい。

【0019】本発明においてガラスの脆さを示す指標値としてはローンらによって提案された脆さ指標値Bを使用する（B.R.Lawn and D.B.Marshall, J.Am.Ceram.Soc.,62(7-8)347-350(1979)）。ここで、脆さ指標値Bは材料のビッカース硬さH_vと破壊靱性値K_cから数1により定義される。

【0020】

【数1】$B=H_v/K_c$　　（1）

【0021】本発明のガラスの脆さ指標値は7400$m^{-1/2}$以下であることが好ましく、より好ましくは7300$m^{-1/2}$以下である。また、本発明のガラスは、化学強化が可能である。化学強化は通常、硝酸カリウム融液もしくは、硝酸カリウムと硝酸ナトリウムの混合融液にガラス板を浸漬することによって行われる。本発明のガラスにおいては化学強化によって、表面から5μm以上、特には10μm以上の厚さの圧縮圧力層を生じさせることができる。

【0022】上述のように本発明のガラスは、傷がつきにくいうえ、従来の磁気ディスク用ガラスと同等以上の化学強化が可能であるため、製造工程中や、製品として使用中の破損おそれを大幅に減じることができる。なお、本発明のガラスは典型的には密度が2．7g／cc以下、特には2．6g／cc以下である。このことも落下時の衝撃を小さくし、破損のおそれを小さくしている。

【0023】また、本発明のガラスの1つの重要な特徴として、フロート成形が可能なことがある。すなわち、フロート成形時の成形温度である10^4ポイズの粘性を示す温度に比べて失透温度が低い。従って、失透などの

不具合を生じることなく、フロート成形が可能である。

【００２４】本発明のガラスは、たとえば、次のような方法で製造できる。すなわち、通常使用される各成分の原料を目標成分になるように調合し、これを熔解炉に連続的に投入し、１５００～１６００℃に加熱して、熔融する。この熔融ガラスをフロート法により所定の板厚に成形し、徐冷後切断する。

【００２５】本発明のガラス基板においては、所定のサイズに切断されたガラス板を化学強化処理する。化学強化処理は公知の方法で行えばよい。すなわち、４００～５３０℃の硝酸カリウムまたはこれと硝酸ナトリウムとの混合液にガラス物品を２～２０時間程度浸漬した後取り出し、徐冷することにより行える。

【００２６】本発明の磁気ディスク用ガラス基板によって、磁気ディスクを形成するには、ガラス基板の上に順次、下地層、磁性層、保護層、潤滑層を設ければよい。

【００２７】本発明で用いられる磁気記録層としての磁性層としては、Ｃｏ－Ｃｒ系、Ｃｏ－Ｃｒ－Ｐｔ系、Ｃｏ－Ｎｉ－Ｃｒ系、Ｃｏ－Ｎｉ－Ｃｒ－Ｐｔ系、Ｃｏ－Ｎｉ－Ｐｔ系、Ｃｏ－Ｃｒ－Ｔａ系などのＣｏ系合金を好ましく採用できる。耐久性や磁気特性を向上するために、磁性層の下に設けられる下地層としては、Ｎｉ層、Ｎｉ－Ｐ層、Ｃｒ層、SiO_2層などを採用できる。

【００２８】本発明では、Ｃｒ層、Ｃｒ合金層、他の材料からなる金属または合金層を磁性層の上または下に設けうる。

【００２９】保護層としては、５０～１０００Åの厚みのカーボンまたはシリカの層が使用でき、潤滑層を形成するためには、３０Å程度の厚みのパーフルオロポリエーテル系の液体潤滑剤が使用できる。

【００３０】

【実施例】

＜板状ガラスの作成＞表１に示した例１～４の４種類の組成について常法に従い調合・混合し、ガラスバッチを調製した。次いで容量約５００ｍｌのＰｔ－Ｒｈ１０％坩堝にガラスバッチを入れ１５００℃で均質化のため約１時間の撹拌を含め約４時間熔解し、カーボン板上に流し出して板状とし徐冷後、常法に従い切断・研磨して約１ｍｍ厚の板状ガラスサンプルを得た。なお、例１～５は実施例であり、例６、７は比較例である。

【００３１】これらのガラスの失透温度、10^4 ポイズの温度、10^2 ポイズの温度、歪点温度、脆さ指標値を測定し、表１に併記した。ついで例１～５の板状ガラスサンプルを切断・研磨して外径６５ｍｍ、内径２０ｍｍ、厚さ０．６３５ｍｍのドーナツ状の円形ガラスディスク基板を各２０枚作成した。

【００３２】脆さ指標値（単位：$m^{-1/2}$）は次のようにして求めた。脆さ指標値をガラスに適用する際の大きな問題は破壊靱性値K_c が正確に評価しにくいことである。しかし、本出願人は、いくつかの手法を検討した結果、ビッカース圧子を押し込んだときにガラス表面に残る圧子の痕の大きさと痕の四隅から発生するクラックの長さとの関係から脆さを定量的に評価できることを見出している。その関係式は式（２）により定義される。ここで、Ｐはビッカース圧子の押し込み荷重でありａ、ｃは、それぞれ、ビッカース圧痕の対角長および四隅から発生するクラックの長さ（圧子の痕を含む対称な２つのクラックの全長）である。各種ガラスの表面に打ち込んだビッカース圧痕の寸法と数２を用いて、脆さ指標値を評価する。

【００３３】

【数２】

$$c/a = 0.0056B^{2/3}P^{1/6} \qquad (2)$$

【００３４】例７のガラス基板は、脆さ指標値が７４００$m^{-1/2}$を超えるので、傷がつきやすく回転時に破損する確率が大きいことになる。

【００３５】＜化学強化性テスト＞上記ガラスディスクの基板各１０枚について化学強化処理を行った。すなわち、例１～４および例７については４８０℃の熔融硝酸カリウム塩に、また、例６については４５０℃の熔融硝酸カリウム塩に、それぞれ１０時間浸漬し、化学強化処理を行った。上記各ガラスディスク基板について、東芝硝子製の主表面応力計ＦＳＷ－６０にて表面圧縮応力層の厚みを測定した結果を表１に併記する。表から明らかなように本発明によるガラス基板は１０μｍ以上の圧縮応力層を生じさせることができる。

【００３６】＜磁気記録媒体の耐湿テスト＞上記未強化品および強化品のそれぞれの主表面上にスパッタ法により厚さ約５００ÅのＣｒからなる下地層を形成した後、厚さ約６００ÅのＣｏ－３０原子％Ｎｉ合金磁性層を形成し、その上に厚さ約３００Åのカーボン保護膜を形成し、さらにその上にパーフルオロポリエーテル系の液体潤滑剤を塗布することにより磁気記録媒体を得た。これらについて８０℃、９０％ＲＨの雰囲気条件で１００時間保持することにより耐湿テストを実施した。

【００３７】表より明らかなように、本発明によるガラス基板の脆さ指標値は、７４００$m^{-1/2}$以下であり、傷がつきにくい。そのため、スピンドルへの装着その他取扱い時においても傷がつきにくく回転時に破損が起こる等の問題がない。更に、例１～５のガラス基板からなる磁気記録媒体は未強化品、強化品ともに変色が認められなかった。また、失透温度は、フロート法の成形粘度である10^4 ポイズに相当する温度よりも低く、フロート法による製造に好適であることがわかる。

【００３８】一方、例６のガラス基板からなる未強化品磁気記録媒体はディスクの内周および外周の端面から２～３ｍｍの範囲にわたってＣｏ－Ｎｉ合金層とガラスとの界面から面内にかけて変色が認められ、例６のガラス基板からなる強化品磁気記録媒体では同じく１～２ｍｍの範囲にわたって変色が認められた。

【００３９】

【表１】

	例１	例２	例３	例４	例５	例６	例７
SiO_2	65.2	61.7	67.4	63.0	64.2	72.5	48.5
Al_2O_3	4.0	9.4	4.1	6.7	6.7	1.5	14.8
Na_2O	1.9	5.5	4.9	3.4	1.4	13.5	5.3
K_2O	14.1	9.2	10.2	12.2	13.5	0.5	6.5
MgO	4.4	3.6	4.5	3.3	3.6	4.0	3.8
CaO	7.0	4.9	7.2	6.9	7.2	8.0	6.6
SrO	－	1.6	0.4	3.2	2.9	－	7.0
BaO	－	1.2	－	0.6	－	－	5.5
ZrO_2	3.4	2.9	1.3	0.7	0.5	－	2.0
Fe_2O_3	0.1	－	－	－	－	0.1	－
Na_2O+K_2O	16.0	14.7	15.1	15.6	14.9	14.0	11.8
MgO ＋CaO ＋SrO ＋BaO	11.4	11.3	12.1	14.0	13.7	12.0	22.9
MgO ＋CaO	11.4	8.5	11.7	10.2	10.8	12.0	10.4
失透温度（℃）	1140	1163	1120	1138	1159	980	1180
１０^4 ポイズの温度（℃）	1192	1187	1138	1147	1185	1040	1046
１０^2 ポイズの温度（℃）	1590	1618	1578	1578	1616	1460	1444
ガラス転移点（℃）	657	647	623	633	658	540	636
脆さ指標値	7200	7300	7200	7200	7100	7100	7800
圧縮応力層厚さ（μｍ）	10	13	14	13	12	20	18
密度（ｇ／ｃｃ）	2.52	2.55	2.49	2.53	2.51	2.49	2.77
耐湿テストによる変色	無	無	無	無	有	有	無

【００４０】
【発明の効果】本発明の高強度な磁気ディスク用ガラス基板はソーダライムシリカガラスを使用したガラス基板に比べ、傷がつきにくく、耐食性および耐エージング性がきわめて優れる。さらに、本発明の磁気ディスク用ガラス基板は、フロート法による成形にも適するものである。

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【手続補正書】
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【手続補正１】
【補正対象書類名】明細書
【補正対象項目名】００３９
【補正方法】変更
【補正内容】
【００３９】
【表１】

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CaO	7.0	4.9	7.2	6.9	7.2	8.0	6.6
SrO	—	1.6	0.4	3.2	2.9	—	7.0
BaO	—	1.2	—	0.6	—	—	5.5
ZrO_2	3.4	2.9	1.3	0.7	0.5	—	2.0
Fe_2O_3	0.1	—	—	—	—	0.1	—
Na_2O+K_2O	16.0	14.7	15.1	15.6	14.9	14.0	11.8
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密度（ｇ／ｃｃ）	2.52	2.55	2.49	2.53	2.51	2.49	2.77
耐湿テストによる変色	無	無	無	無	無	有	無